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Laboratory Development of a Passive Sampling Device for Hydrazines in Ambient Air

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A passive sampling method applicable to personnel and area monitoring has been developed for the quantitation of hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) in ambient air at the part-per-billion (ppb) level. The method uses a black molded low density polyethylene badge consisting of a diffusion barrier and a citric acid collection medium. It collects samples that can be analyzed by the NIOSH colorimetric method or a coulometric titration procedure. The two millimeter thick diffusion barrier contains 144 one millimeter diameter holes and produces a collection rate for MMH of approximately 27 ml/min. The accuracy of data collected with this badge is within 30% of actual values. The dosimeter has demonstrated accuracy for sampling periods of 15 minutes to 66 hours, when sampling MMH at the threshold limit value (TLV) concentration of 200 ppb. The limits of detection are dictated by the specific analytical method. Coulometric titration will detect exposures of 30 ppb-hours. An evaluation of the effects of face velocity, relative humidity, and potential interferences was conducted.

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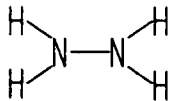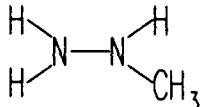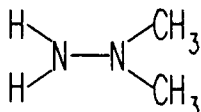Prescribed by ANSI Std Z39-18
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LABORATORY DEVELOPMENT OF A PASSIVE SAMPLING DEVICE FOR HYDRAZINES IN AMBIENT AIR

INTRODUCTION

The potential carcinogenicity of hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) has caused concern for the health and safety of the workers that may come in contact with them. The monitoring of employee exposure and work place contamination is necessary to insure exposure remains below the defined limits and complies with the law. The chemical structures of these compounds, their ACGIH [1] and NIOSH [2] recommended exposure limits, and their diffusion constants are shown in Table 1. Potentially the exposure limits may be lowered to 10 ppb for all three hydrazines [3].

Table 1. Recommended Exposure Levels and Diffusivities for Hydrazine Propellants

Compound	Structure	ACGIH	NIOSH	D (cm^2/s)
Hydrazine		0.1 ppm	0.03 ppm	0.154
Monomethyl Hydrazine		0.2 ppm	0.04 ppm	0.122
Unsymmetrical Dimethylhydrazine		0.5 ppm	0.06 ppm	0.104

The reactivity of the hydrazines and their tendency to undergo oxidative decomposition has hindered the development of detection systems. For convenience, the term "hydrazines", when used in this report, refers to all three of the hydrazines in Table 1. Hydrazines are particularly prone to decompose catalytically on metal surfaces [4]. In order to sample hydrazines, a collection scheme is required with the ability to stabilize hydrazine and its derivatives without interfering with accepted analytical procedures. In addition a personnel dosimeter should be simple, cheap, not sensitive to typical work place interferences and not impede with worker perforr nce.

Current methods of sampling hydrazines involve detector tubes ⌣ midget impingers with an acidic collection solution [5]. These are "active" sampling methods, meaning they involve the use of an air pump to draw the atmosphere through the collection medium. The pumps are bulky, expensive and require a power source for long-term operation, hence they are not ideal for personnel monitoring. Because of these constraints active methods are unsuitable to monitor large areas where many sampling points are required such as the servicing area for the Space Shuttle. It is desirable to monitor this area continuously so that if some hydrazine is accidentally released, the amount and area

affected can be determined. Maintaining a large number of active samplers in this area is not practical. It was the goal of this project to develop a passive dosimeter for hydrazine and MMH in the form of a badge that could be used either as an area monitor or personal sampler.

The first form of a quantitative personal sampling device utilizing passive collection was reported by Palmes and Gunnison in 1973 [6]. In its simplest form it consists of a tube with a collecting substance at the bottom. This type of sampler is often referred to as a "Palmes' tube" and has been found to behave ideally when the area to length ratio of the tube (A/L) is less than 0.1 cm [7]. Another passive sampler design in the form of a badge is shown in Figure 1. Ideally the diffusion barrier/draft shield is constructed so that the sampling rate only depends upon diffusion and is independent of the flow rate of the ambient air. Some designs incorporate a screen that can hold a loose collection medium such as activated charcoal in place [8,9]. The screen can also serve as the diffusion barrier. These types of devices are available commercially [10]. Such a system is not suitable for hydrazine collection [11].
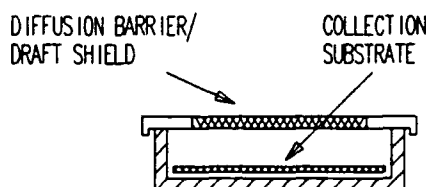

Figure 1. Schematic of a passive badge.

Due to the reactivity of hydrazine the choice materials for the badge design is limited. For instance it is not possible to use metal screens as a diffusion barrier/draft shield. Porous perfluoro polymers, such as *GoreTex*, cannot be used due to their large surface area. The behavior of low concentrations hydrazine with various materials has been previously studied at this Laboratory [12]. The only suitable materials of construction for a diffusion barrier are perfluoro polymers, polyethylene, and polypropylene. In addition to inertness, the diffusion barrier must sample at a rate high enough to collect sufficient material for measurement in a reasonable time. This is a stringent requirement as the TLV values for hydrazines are so low.

THEORY

Before discussing our particular badge design, it is worthwhile to review the theory of passive sampling. For an ideal badge design the mass sampling rate (M) of the passive collector depends only upon the diffusion coefficient (D) of the analyte as described by Fick's first law of diffusion integrated for a tube [13].

$$M = D \, (A/L) \, (C_1 - C_2) \tag{1}$$

Where: A = The area of the diffusion channel;
L = The length of the diffusion channel;
C_1 = The external (ambient) concentration of the analyte; and
C_2 = The gas-phase concentration of the analyte at the surface of the collector

Hence the diffusive conductance (C_d) is merely:

$$C_d = D \, (A/L) \quad (cm^3/s) \tag{2}$$

Typically D is in cgs units. For our final badge design, that has a diffusion barrier consisting of 144 one mm diameter by two mm long holes, the C_d is 0.85 cm^3/s based on a diffusion constant of 0.15 cm^2/s. Including the conductance of the air gap of the badge, the net sampling rate is 0.79 cm^3/s. The total conductance is the inverse of the sum of the inverses of the individual conductances when calculating conductances in series. These and subsequent calculations are based upon a diffusion constant of 0.15 cm^2/sec, one atmosphere pressure and 25°C. Additionally it is assumed that the concentration at surface of the collection medium is zero. Note the amount of material collected does not depend upon the ambient pressure and only depends upon the square root of temperature; thus these parameters can be neglected when performing diffusive sampling.

In contrast to equation 1, where diffusion is proportional to the area of the hole, the viscous flow conductance (C_v) is proportional to the area squared. In similar terms to equation 2, the Poiseuille equation can be reduced to equation 3 for flow at an average pressure of one atmosphere [13].

$$C_v = 2.2 \times 10^8 \, (A^2/L) \quad (cm^3/s/atm) \tag{3}$$

The mass flow is obtained by multiplying C_v by the gas concentration and the pressure difference. The advantage of using many small holes is based upon the fact that viscous flow is proportional to A^2/L; whereas diffusive flow is proportional to A/L, see equation 1. Thus increasing the number of holes of the diffusion barrier of the badge, while keeping the total area of the holes constant, decreases the viscous conductance in proportion to the number of holes without affecting the diffusion rate. The principal assumption made using equations 1 and 3 is that these holes can be treated as tubes. This situation has been treated theoretically [14] and would reduce the viscous conductance by about factor of two.

Because of the magnitude of the constant in equation 3, it is understandable that viscous flow could have a large effect on the collection rate. For example, assume that there is a pressure imbalance across the badge face. Based on equation 3 a pressure difference on the order of 10^{-5} atmospheres would be sufficient to cause a flow of 1 cm^3/s through ten of the holes. Although this pressure may seem extraordinary low, it should be compared to the pressure necessary to produce the flow in the one of the chambers used to measure the badge performance. The chamber is 10 cm diameter by 30 cm long and had a flow rate of 5 l/min. Based on equation 3, a pressure gradient of 10^{-9} atm would be sufficient to produce this flow. Thus in a normal environment there would be a negligible pressure difference across the badge face due to laminar flow across it. There might be some turbulence at the surface of the badge due to the holes that could result in slight pressure differences sufficient to induce flow through the holes. Thus reducing the C_v of the badge is important and having the badge face smooth would lessen this effect. Both are achieved by having a large number of small holes.

In order for the sampling rate of the badge to be independent of face velocity, the rate at which the sample can be transferred from the atmosphere to the badge should be much greater than the badge sampling rate. It is important to calculate this rate at low flows. At low flows the total conductance to the badge, C_t, is determined by two mechanisms: a pure diffusive term, C_d, that is independent of flow; and a convective term, C_c, that depends on the face velocity.

$$C_t = C_d + C_c \tag{4}$$

The diffusive term can be calculated from equation 2, assuming a face diameter of 2.5 cm and a length of 2.0 cm. This results in a flow rate of about 0.5 cm³/s for the diffusive term. Thus at the lowest face velocities the net sampling rate of the badge would be 0.3 cm/sec due to the C_d terms from equations 2 and 4.

Calculation of the convective term follows the method given by Bennett and Myers [15].

$$C_c = 0.66 \, D \, (A/x) \, (Re_L)^{0.5} \, (Sc)^{0.33} \tag{5}$$

Where: x = diameter of the badge face
Re_L = the Reynold's number for flow along a surface
Sc = the Schmidt number

This equation is for a wide plate and ignores edge effects; neither assumption is valid for our badge which is disk shaped. A disk would have a higher sampling rate; hence equation 5 provides a lower bound for the convective sampling rate. The Schmidt number, which is the ratio of viscosity to the product of the diffusion constant and the density, is about one. The Reynold's number is product of x, gas velocity, and density divided by gas viscosity. For our case the Reynold's number is about 1.5 times the gas velocity (v) in cm/s. Hence equation 5 can be simplified to:

$$C_c = 0.88 \, D \, (A/x) \, v^{0.5} \tag{6}$$

Substituting the dimensions of our badge:

$$C_c = 2.6 \, v^{0.5} \tag{7}$$

Thus the sampling rate of the badge will be dominated by the convective term until the gas velocity is less than 1 cm/s (2 ft/min). Since typical work place air velocities are 25-40 cm/s [11], the convective term will dominate equation 4 and the sampling rate of the badge is only dependent upon the conductance of the diffusion barrier.

EXPERIMENTAL

Experimental Set-Up. The reactivity of the hydrazines makes it difficult to generate and maintain the low ppb levels required for testing. A dynamic system, Figure 3, was assembled which supplies concentrations from approximately 0.1 to 10 times the TLV for each compound. Diffusion tubes

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housed in a constant temperature bath, and continually purged with 100 ml/min of dry nitrogen provide the hydrazine vapors [16]. The desired concentration is obtained by adjusting the temperature of the bath, the size of the diffusion capillary, and/or the amount of dilution air.

Conditioned house-compressed air is used as the diluent. The conditioning procedure consists of passing the house air through a series of demisters, a hot Hopcalite catalyst bed, a reciprocating dual-tower molecular sieve scrubber, and finally through a canister containing potassium per-mangenate coated alumina (Purafil) and charcoal. The cleaned air is humidified using a stainless steel gas washer (bubbler) containing distilled, deionized water. Control of the relative humidity is achieved by varying both the gas washer head pressure and the ratio of the humidified to dry air. The moisture content of the air is measured by a hygrometer. The dilution air is selected and monitored using calibrated mass flow controllers capable of providing 0 to 10 l/min. This apparatus is similar to one constructed previously at this laboratory [17].
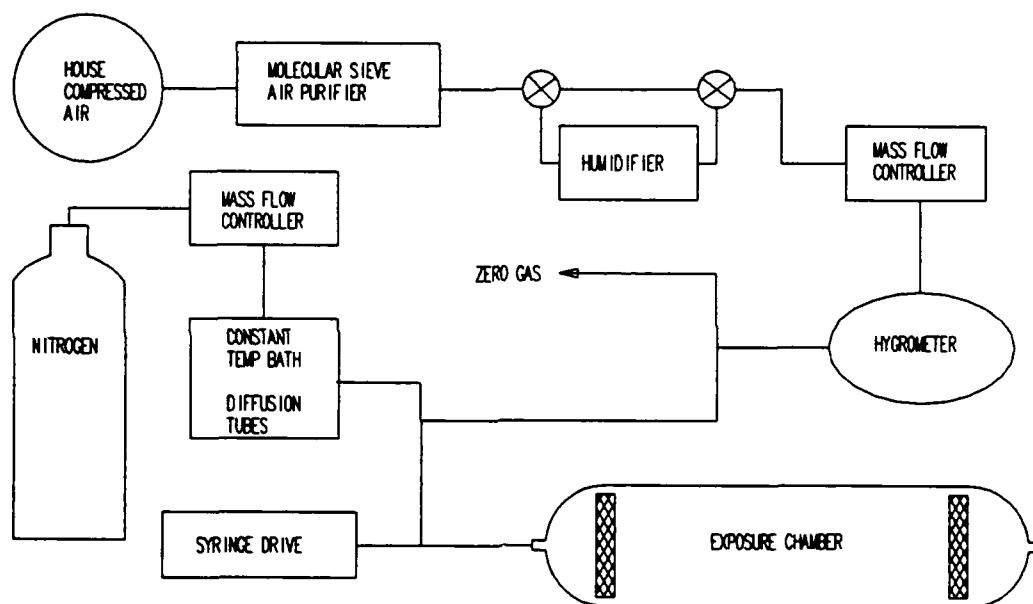

Figure 3. Test gas generator schematic.

The concentration of the test atmosphere was verified before and after each exposure by standard wet chemical techniques. Liquid impinger samples were collected and analyzed by coulometric titration [18] or colorimetric procedures [5]. In addition, a chemiluminescence instru-ment, Thermedics Model 141, and a paper-tape instrument MDA Model 7100 were occasionally used to monitor the gas stream.

The experiments were conducted in three glass exposure chambers, one of which is depicted in Figure 4. They were cylindrical with hemispherical ends. The exhaust end was removable to allow insertion of the samplers. Teflon baffles placed at each end were used to induce laminar flow. The internal diameter of each chamber was different in order to allow us to study a variety of the face velocities while holding other gas stream conditions constant. Further variation in face velocity

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could be attained by varying the volume of dilution air in combination with substituting chambers. Table 2 lists the statistics of the chambers available for testing.
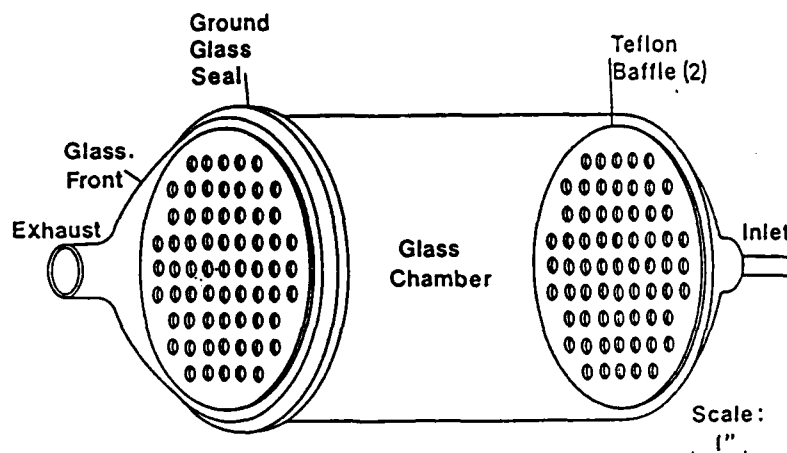

Figure 4. Glass exposure chamber used for laboratory badge testing.

Table 2. Size of the Gas Exposure Chambers and Typical Conditions.

Diameter	Area	Flow	Face velocity*	
5.5 cm	23.8 cm^2	5 l/min	275 cm/min	(9.0 ft/min)
9.0 cm	63.6 cm^2	5 l/min	86 cm/min	(2.8 ft/min)
14 cm	154 cm^2	10 l/min	67 cm/min	(2.2 ft/min)

*The badge area of 5.6 cm^2 (viewed from the side) reduces the effective cross sectional area of the chambers. The face velocity calculations were carried out using the adjusted chamber area. Note these are average velocities, since the gas velocity profile will be a maximum at the center of the chamber [19].

Fabrication of the Passive Sampler. The prototype sampler was made by placing a collection disk into a housing similar to Figure 1. The badge housing consisted of three parts: base, spacer, and machined diffusor. As discussed in the introduction, the diffusor is the most critical portion of the housing. It controls the collection rate and minimizes dependence upon the ambient face velocity. Various designs for diffusers were tried. The number and size of holes was varied while maintaining a constant total hole area. Tests were conducted on a series of badges machined with hole sizes of 1.0, 1.5, and 2.0 mm in diameter. The number of holes on each diffusor was 140, 76, and 35 respectively. Several styles were machined and tested. The machined samples were prepared from chlorofluoro polymers (Kel-F) [20], polypropylene, and teflon in order to examine material dependencies.

Based upon the results obtained with the prototype badge, a new badge was designed suitable for molding and mass production. A drawing of the design is shown in Figure 5. The badge was

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HOLE PATTERN

27mm

2mm

SPACER
SIDE VIEW

30mm
40mm

SPACER
TOP VIEW

47mm
43mm
39mm
27mm

6mm
4mm
2mm

DIFFUSION BARRIER
SIDE VIEW

4.5mm
9.5mm
14mm

40mm
43mm
47mm

BASE
TOP VIEW

47mm
43mm
40mm

6mm
4mm
2mm

BASE
SIDE VIEW

14mm
9.5mm
4.5mm

47mm
43mm
42mm

CAP
BOTTOM VIEW

47mm
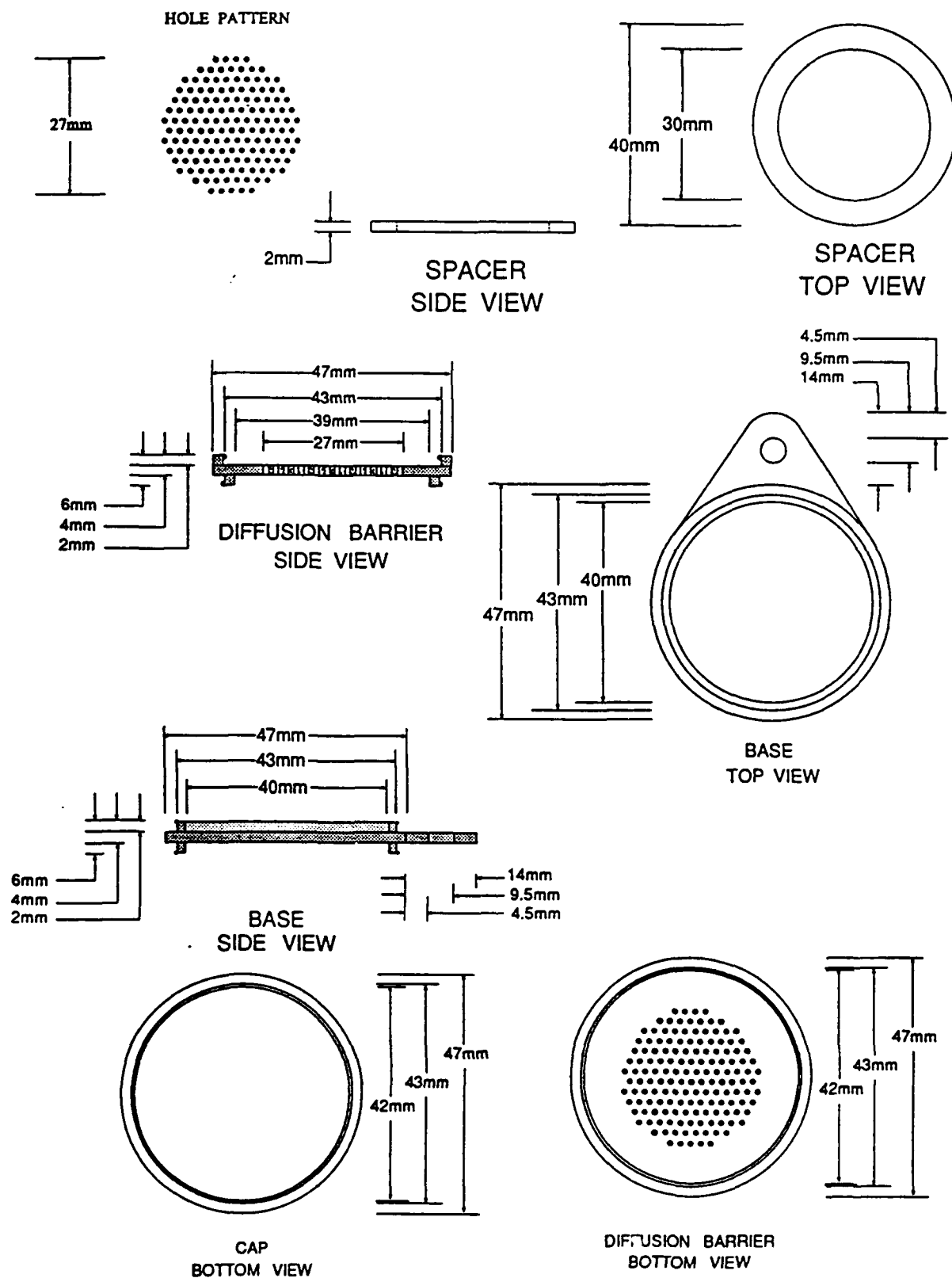43mm
42mm

DIFFUSION BARRIER
BOTTOM VIEW

Figure 5. Design and dimensions of the complete badge.

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produced by Moldsavers, Inc of Miami, Florida and made of low density polyethylene. The first lot was colorless which worked well in the laboratory; after field testing revealed a sunlight problem, a second lot was molded from black low density polyethylene. Moldsavers was unable to cast the badge in polypropylene or Kel-F due to these plastics sticking to the diffusor mold.

The molded badge housing consists of four pieces: the base, spacer, diffusor, and cap. The cap may be snapped on the back of the base during badge exposure and snapped over the diffusor for storage. The spacer holds the collection substrate against the bottom of the base. The diffusers were designed so that two or more could be snapped on top of each other to reduce the sampling rate if desired. A slight modification was made to the diffusor for production purposes. Three of the holes were moved from the center of the disk to the edge of the hole pattern. The solid areas that replaced the holes were needed for injection of the plastic and removal from the mold.

Collection disk. The collection disk is placed in the base of the badge housing and held in place with the spacer. Initially, we tried etched-glass disks coated with concentrated sulfuric acid solutions as a collection medium. These are messy and did not stabilize MMH well. We found that plastic disks coated with citric acid were a much better collection medium. Eventually we discovered that filter paper was superior to plastic as a substrate for citric acid. Citric acid was selected as the coating agent for its properties as an acid and an antioxidant.

The disk is coated by dipping it into a citric acid monohydrate (CA) solution. Citric acid is dissolved in methanol to form a 30% (gm/cm^3) solution. This solution has been tested for its coating abilities and performance during an aging period. The aging period is defined as the time interval between the preparation of the solution and its use as a coating. Preliminary results indicated that the formation of methyl esters of the citric acid caused the coating properties to change. At an age of one to two weeks the solution was found to have the best performance when coated on the polyester substrate [21]. If the solution was used at any other time, the citric acid tended to crystallize on the surface of the substrate. The properly aged solution will be referred to as the standard or control coating. Most testing was conducted with the standard coating. An experiment was conducted on the ability to preserve the standard coating by refrigeration to retard the formation of esters.

It is desirable to have a solution that does not require aging. To facilitate this, variations of the standard coating recipe were tested. Solutions were prepared where a percentage of the methanol (MeOH) solvent was replaced with water, Table 3. The percent water was calculated using a total volume of 25 ml of solution (solvent and solute). The citric acid and water were combined and the solutions were adjusted to the 25 ml mark with methanol. The 7.5 grams of citric acid displaced approximately 2.5 ml of solution, therefore the solution referred to as 90% water contained no methanol.

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Table 3. Solutions Prepared with Water

% Water*	(ml)	Citric Acid (g)
1	0.25	7.5
5	1.25	7.5
10	2.5	7.5
25	6.25	7.5
50	12.5	7.5
75	18.75	7.5
90	22.75	7.5

* Percentage water based on 25 ml total volume.

In addition, tests were conducted on solutions prepared with isopropanol (IPOH), with and without stoichiometric amounts of methanol. The methanol was added to allow formation of the methyl esters. By this technique, the ratio of methyl ester to acid could be controlled and solutions prepared to simulate the standard solution at various stages of aging. In some cases, an acid was added to catalyze the ester formation. We hoped to synthesize the ideally aged standard coating which could be used immediately. Table 4 outlines the coating solution variations examined.

Table 4. Coating Solutions Used in Aging Study.

	MeOH	CA (H_2O)IPOH		Additive
g/mol	32	210		
g/ml	0.79			
MeOH : CA	ml	gm	ml	
1:1	0.61	5.04	15	
1:1	0.61	5.04	15	H_2SO_4 (one drop)
1:1	0.61	5.04	15	H_2O 0.5 ml
1:4	0.15	5.04	15	
Control 3:1	15	5.04	0	

Glass, polyester, and paper have been investigated as collection disk substrate. The glass was obtained in etched disks with a diameter of 4 cm. The polyester disks were cut from sheets of matted drafting film [22]. The paper was Whatman #42 filter paper purchased as 4.25 cm diameter disks [23]. The substrate disks were coated by immersion in the citric acid solution. Teflon-coated tweezers are used to remove the disks. As a precaution, to avoid the potential for metal-catalyzed

decomposition of the hydrazines, no metals are allowed to come in contact with the solution. Large quantities of the coated paper disks were prepared in the citric acid solution, placed on a clean surface, and allowed to dry. They could be used immediately or stored in plastic badges for future use. As discussed later, they should be stored in the dark and as a precaution in a refrigerator.

The use of paper as a substrate inhibited the crystallization of the citric acid coating. With this feature we thought it may be possible to use coating solution that was not aged for the seven days. Tests were conducted to monitor the effects the aging process had upon the performance of the citric acid solution coated on the paper substrate.

Experimental Conditions. Standard exposure conditions that were: 200 ppb MMH, 35% to 45% RH, and at a face velocity of 86 cm/min (2.8 ft/min). These condition were used for the evaluation of the badge unless otherwise noted. Most of this work was with MMH because it is the hydrazine used in greatest quantity by NASA and is the most prone to decomposition on surfaces or in solution [24]. The sampling rates of the diffusors were calculated from a series of experiments. Standard exposure conditions were used for exposure periods of 0.25 to 66 hours.

The effects of face velocity upon the collection rate of the badges was tested with a MMH gas stream at face velocities between 86 and 670 cm/min. The test atmosphere was dry air contaminated with approximately 200 ppb MMH. The badges were exposed for five hours. Bare collection disks (no diffusors) were tested along with a variety of diffusor styles. The final black badge design was spot checked at 86 and 170 cm/min face velocities only.

The linearity and reproducibility of the molded prototype sampler was examined by exposure to a variety of equivalent combinations of time and concentration. For example, 1 hour at 600 ppb MMH = 3 hours at 200 ppb = 0.6 ppm hours. Exposure times ranged from 0.25 to 65 hours and standard face velocity and RH were used.

Interference effects from isopropanol, ammonia, and Freon (mixture of Freon 11, 12, and 114) were investigated using the Kel-F badge and polyester substrate. The ammonia (50 ppm) and Freon mix (50 ppm each) containing gas streams were generated by dilution of mixtures from analyzed gas cylinders. The isopropanol containing gas stream (500 ppm) was obtained by volatilization of the liquid injected into the clean air flow by an automated syringe.

Analytical Procedure. The methods used for quantitation of the hydrazines have been described in detail [25]. The coated substrate is removed from the housing assembly with teflon-coated tweezers and placed in a glass container. The analyte is desorbed from the disk for approximately 20 minutes. The desorption time required for the paper substrate was examined by analyzing aliquots of a sample during the desorption period. The solution obtained after desorption is treated as a liquid sample and analyzed using any of the accepted analytical methods may be used [5]. The solvent system and the amount used for desorption is dictated by the analytical method selected. Initially, three methods were examined, phosphomolybdic acid (PMA) and para-N,N-dimethylaminobenzaldehyde (PDAB) colorimetric procedures and the coulometric titration procedure.

RESULTS AND DISCUSSION

In order to determine the maximum rate that the badge could sample bare coated substrate disks were placed in the chamber. Duplicate samples were collected at two flow rates, two humidities and three times. The gas contained 100 ppb of hydrazine. The results are shown in Figure 6. The data shows no dependence upon humidity. Based upon equation 7 and a flow of 5 cm/sec (10 ft/min), the minimum collection rate for one side of the disk should be 5.8 ml/s. Since both sides of the disk would collect the sample, the rate would be twice this or 11.6 ml/s or 700 ml/min. At a flow rate of 1.2 cm/sec (2.5 ft/min) the calculated collection rate is 350 ml/min. The measured rates of 318 ± 30 ml/min and 927 ± 95 ml/min compare quite well with these calculated rates. It is interesting that the measured velocity dependence has a 0.8 power dependence which is what would be expected in a turbulent environment [26].
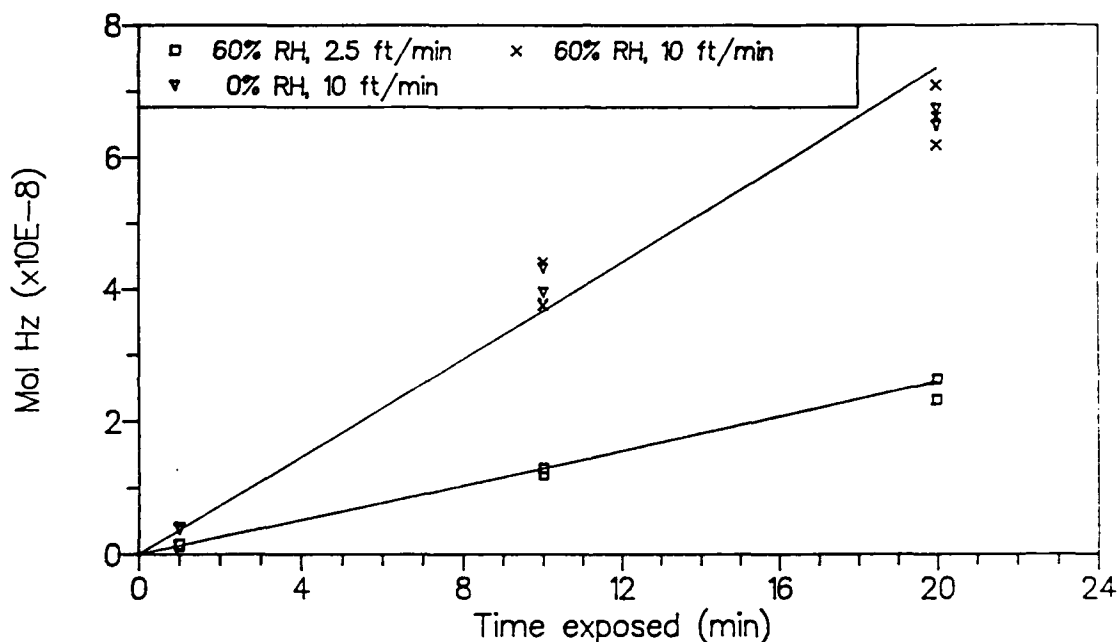

Figure 6. Collection rate of a bare disk.

The main result of this experiment is that the transport rate to the face of the badge is much greater than the sampling rate of the badge in accord with theory. Thus for all real environments the sampling rate of the badge will only be determined by diffusion through the badge face. This experiment also shows there is no dependence on the collection rate of the disk with humidity and that rate is rapid implying that the sticking probability of hydrazine on the disk is close to one.

Based on a collection rate of 1000 ml/min and a detection limit of 0.1 μg of MMH by coulometry, an exposure dose of one ppb-hr could be detected using a bare disk. Thus bare disks could be used as a very sensitive method to determine hydrazine exposure and could be useful in setting an upper limit to the concentration in an environment. The user must be aware, however, of the strong dependence of sampling rate on ambient air velocity. Additionally it should be possible to use coated

disks as quantitative collectors by pulling a known volume of air through them. Based upon other work at this Laboratory, a rate of 5 l/min is feasible. The detection limit would be about one ppb of MMH for a 10 min sample.

Badges were produced with diffusion barriers with hole sizes of 2, 1.5 and 1 mm diameter. Within experimental error no significant differences in the sampling rate or face velocity dependence were observed. Since the use of small holes can reduce the effect of viscous flow, a prototype design was selected having a 2.5 cm diameter pattern of 144 one millimeter diameter holes. This was the smallest size which we believed practicable to machine and is practicable to mold as we later discovered.

The material dependency was examined by testing badges produced from polypropylene, Teflon and Kel-F. The badges made from polypropylene and Teflon were machined from solid rods of the respective material. Some of the data obtained with these systems is shown in Figure 7. The calculated average collection rate is plotted against the exposure time. The machined badge housings deviated from linearity especially at low concentrations and higher humidities. Adsorption of the hydrazines into the sintered teflon stock and the tool marks from machining were thought to be responsible. Performance improved with the use of a molded Kel-F badge housing with drilled holes. This data is summarized in Table 5.

Table 5. Time in Hours to Reach Fraction of Maximum Collection Rate.

Material	Time to reach 50%		Time to reach 80%	
	Dry	45% RH	Dry	45% RH
Kel-F	0.2	0.5	1	2
Polyprop.	1	3	4	8
Teflon	3	8	6	>16

The reason for the lower collection rate at shorter times is assumed to be that the badge material depletes the hydrazine concentration by absorbing the hydrazine on the surfaces of the badge including the walls of the holes. A simple model can be constructed assuming that the absorption on the walls follows an standard Langmuir equation [27]. Based on this assumption, the instantaneous sampling rate (R) of the badge as a function of time is given by the following equation:

$$R = R_M(1-e^{-At}) \tag{8}$$

Where: R_M = The maximum rate reached after equilibration; and
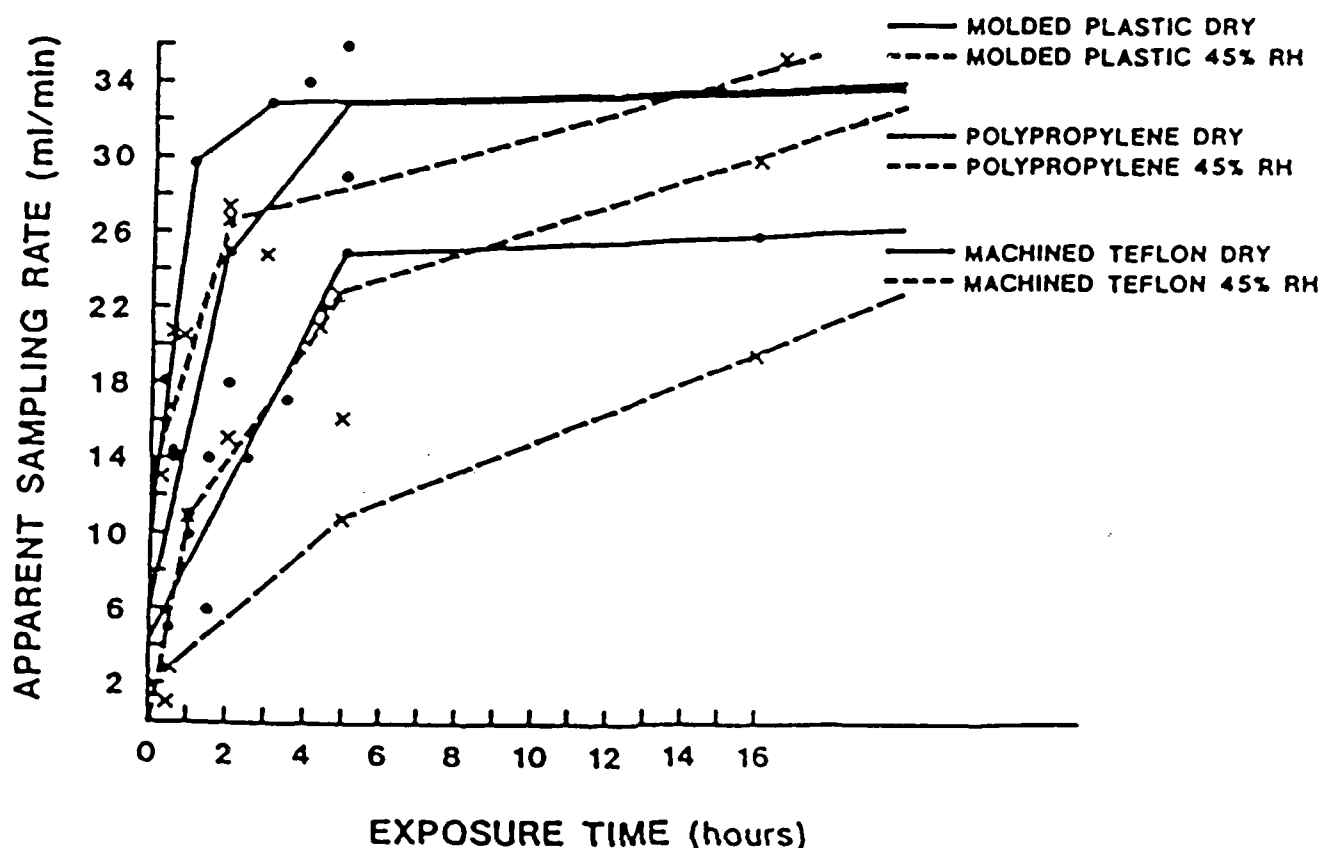 A = the time constant of the absorption on the walls

Figure 7. Average collection rate as a function of time.

If equation 8 integrated from time 0 to time T, then the average rate (R_A), which is the rate measured in the experiment, is given by:

$$R_A = R_M(1+(e^{-AT}-1)/(AT)) \tag{9}$$

As an example using data for Kel-F in Table 5, it takes about 0.5 hr to reach an average rate of 50% of the maximum for 45% RH. Thus R_A/R_M equals 0.5 and T equals 0.5 hr in equation 9. Since this is a transcendental equation, it must be solved numerically for A, which in this case is 3.2/hr. Substituting this value into equation 8, the instantaneous rate at 0.5 hr is 0.8 of the final rate. The Kel-F badge was tested at different face velocity conditions; this data is presented in Table 6. There is no apparent face velocity affect using this badge design.

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Table 6. Face Velocity Test Data.

Exposure Time (hrs)	Relative Humidity (%RH)	Face Velocity (cm/s)	MMH (ppb) concentration	Sample Rate (ml/min)
3	65	2.5	180	29
3	65	10	179	30
64	25	1	189	27
64	25	2.5	173	26

The Kel-F badge was used for interference testing. The interfering compounds are ones that could be present in operations at the Kennedy Space Center. The data obtained is presented in Table 7. It should be noted that the scatter in the data falls within the precision expected for this sampling technique.

Table 7. Interference Testing.

MMH * (ppb)	Interfering Compound (ppm)	Measured Sampling Rate ml/min (% change)
174	IPOH, 500	30
188	Ammonia, 50	25
176	Freons, 15	29

*Two hour exposure with 65% RH at 5.2 ft/min.

The molded badge was tested to determine the sampling rate at the TLV level of MMH and 40% RH. The data is summarized in Table 8. The average rate of 27 ml/min is lower than the theoretical rate of 38 ml/min. The most plausible reason for the difference would be that the concentration of the MMH at the surface of the substrate is not zero but about 29% of the sample concentration, that is C_2 is 29% of C_1 in equation 1. The lower rate at 0.25 hours is due to both equilibration of the badge surface and the chamber surfaces after the chamber was opened to insert the badges. The badge certainly has reached 80% of the maximum rate within 15 min. Based on equations 8 and 9 the time for the instantaneous sampling rate to be 50% of the maximum is less than 2 minutes. The drop off in sampling rate for the 65 hr sample is due to storage problem of the substrate, see below. The total dose collected corresponds to a range of 3.2 to 880 nmol of MMH. This data also shows there is no dependence of the collection rate upon dose collected in this range. Based on a detection limit of MMH of 0.1 μg, the minimum detectable dose is 30 ppb-hr.

Table 8. Badge Sampling Rate.

MMH Conc. (ppb)	Time (hrs)	Measured Rate (ml/min)
215	0.25	24
215	0.25	20
215	0.25	29
212	0.67	28
212	0.67	31
192	4.0	22
192	4.0	26
192	4.0	30
187	5.0	27
187	5.0	27
187	5.0	29
225	18	29
225	18	26
237	65	23
237	65	23
	Average*	27.5
	Std. Dev.*	2.4

*The data for 0.25 hrs and 65 hrs was not used (see text).

The fall off in sampling rate at longer sampling times was traced to storage problems of the MMH on the citric acid coated polyester substrate. We had used the polyester drafting paper as the citric acid solution wet it uniformly since its surface texture was designed for inking. We did not realize that would cause long term storage problems. The original storage tests were performed using a glass substrate, and did not indicate any problem with storage stability. This data is shown in Table 9 which shows the results from the original tests. In each test four badges were exposed to MMH, two of the badges were analyzed immediately and two were stored in the dark until analysis. No storage problem was found in either test. Glass disks are not a desirable substrate since they are fragile and have an uncertain availability. We used disks in from our stockroom which had been ordered many years ago. We do not know the source and could not find any listed in several different catalogs.

Table 9. Storage Tests.

MMH Conc. (ppb)	Days Stored	Sample Rate (ml/min)
Test 1 - Exposure time 18 hrs		
242	0	26
242	0	24
242	3	28
242	3	24
Test 2 - Exposure time 5 hrs		
268	0	26
268	0	24
268	5	31
268	7	27

Investigations were conducted to find an alternate substrate for the polyester due the poor stability of the trapped MMH. Many materials were investigated, including filter paper, fiber glass, and porous membranes made of a variety of materials. The filter paper was the most promising. It was investigated and compared to polyester. The collection performance of the two substrates was similar. The room temperature storage stability of the paper was much greater than that of the polyester. This data is shown in Table 10.

Table 10. Paper Storage

Days Stored	Per Cent of Theoretical
8	74
8	74
10	85
10	86
10	86
12	103

MMH = 194 ppb, RH = 65%

In comparison, the polyester substrate retains between 10 to 50% of the amount of MMH sampled after one week of storage. We hypothesize that the MMH was reacting with the carbon oxygen double bond of the ester linkage of the polymer. Since the citric acid coated paper worked so well, uncoated paper was tried as a substrate. This test was unsuccessful as the paper only retained 30% of the MMH after one day of storage. The citric acid coated substrate was tested with all three analytical methods. No difference or interference problem was found. Exposed badges were stored

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in an oven at 38°C (100 °F) for 24 hrs., no decrease in the stored hydrazine was detected. In addition to badge storage, the storage of the extracted solution was investigated. The collection disk was placed in a glass vial with 15 ml of 0.1 M H_2SO_4, capped and stored in the dark or on the bench top until analysis. Storage tests of the extracted solution have been conducted for periods approaching three months. Again no significant change was observed.

The performance of the citric acid solution coated on the paper substrate was monitored during the aging process. A solution was prepared but not set aside for aging. On days 0 (day of preparation) through 4, 7, 8, and 14 the coating solution was used to prepare 6 badges. The molded polyethylene housing was used. The badges were exposed to the standard MMH testing conditions. Three were analyzed immediately following exposure, the others were held for storage stability testing. No significant difference was detected. Thus the age of the citric acid solution is not important for paper substrate. Currently we know of no reason why paper cannot be used exclusively for the badge substrate. We have discussed the aging process of the citric acid solution in the event that a different badge substrate is used in the future which may require aged solution. Potentially a different substrate might be needed to be compatible with a future analytical method.

The prototype system has demonstrated a detection limit of 15 minutes of TLV exposure when analyzed with the coulometric titration method. We were unable to define a lower limit experimentally due to the time required to equilibrate the test atmosphere.

At the end of this development these badges were field tested at the Kennedy Space Center. The field test is reported in detail in a separate report [25]. The principal discovery was an interference to analysis using coulometry. The interference was determined to be caused by sunlight irradiating the badge. This effect had not been observed in tests on the roof of the Chemistry building at NRL. These tests were conducted in the fall and winter when there is negligible amount of UV radiation transmitted by the atmosphere [28]. In order to decrease this effect, a new set of badges was molded from black polyethylene. Using these badges the effect of sunlight was marginal [25]. Laboratory tests of the black badges showed them to perform comparable to white badges. In one test exposed badges were stored for 6 weeks at room temperature. No loss of MMH was detected.

CONCLUSIONS

A passive dosimeter has been developed for hydrazines. The dosimeter overcomes problems caused by the reactivity of the hydrazines by molding a dosimeter from polyethylene and a collection disk made from filter paper coated with a citric acid solution. This coating has shown an ability to trap and stabilize the hydrazines without interfering with colorimetric or coulometric quantitation procedures. TLV levels of MMH can be detected for exposures as short as 15 minutes.

The paper substrate system has additional advantages. It has demonstrated room temperature stability of the trapped analyte for periods greater than one week, and high temperature stability for 24 hours. This was not possible with the polyester substrate. Storage of the polyester system must take place in the freezer, or the analyte must be desorbed and stored as an extracted solution. This would not allow the badge to be used to measure a time-weighted-average (TWA) exposures for

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periods any greater than one work day. With the use of a paper substrate, the period of use can be extended to one week if needed. A badge could be placed in an area, or dispensed to an employee at the beginning of a work shift on a Monday, and collected for analysis at the end of the work day on Friday.

The molded low density polyethylene badge provides an excellent housing for the collection disk. A molded housing has many advantages over the machined badge. The resulting product is cost effective at $0.10 per unit. The molding process reduces the available surface area, which decreases the amount of analyte lost by adsorption into the badge housing. In addition, the badge-to-badge reproducibility is better because of identical diffusion barriers. The diffusor minimizes face velocity effects while retaining a detection limit of 15 minutes for 200 ppb MMH contaminated air. The assembly of the badge is simplified by its ability to be securely snapped together. Once snapped in place, the cap protects the badge from exposure to analyte. The resulting badge has the desirable qualities of a disposable personal dosimeter. It is durable, inexpensive, and lightweight.

The sampler must be returned to a laboratory for analysis where NIOSH recommended procedures may be used to quantitate the extract. The data obtained from the paper substrate system is acceptable for TWA exposure documentation. We envision a final design of the hydrazine dosimeter as being a combination of the badge described and a colorimetric real-time indicator. The indicator would serve as a warning system for the user and as a dose estimator for the analytical laboratory.

REFERENCES

1. DHEW (NIOSH) Publication No 78-210.

2. DHEW (NIOSH) Publication No 78-172.

3. ACGIH report on proposed and current changes to TLV and BEI lists, 21 May 1989.

4. E. W. Schmidt, *Hydrazine and its Derivatives*, (John Wiley, New York, 1984), Chap. 5.

5. *NIOSH Manual of Analytical Methods, 2nd ed.*, DHEW(NIOSH), Cincinnati, OH, 1977, Vol 3, Publication 77-157c.

6. E. D. Palmes and A. F. Gunnison, *Amer. Ind. Hyg. Ass. J.* 34, 78-81 (1973).

7. E. D. Palmes and A. F. Gunnison, *Amer. Ind. Hyg. Ass. J.* 37, 570-577 (1976).

8. W. J. Lautenberger, E. V. Kring, and J. A. Morello, *Ann. Am. Conf. Gov. Ind. Hyg.* 1, 91-99 (1981).

9. V. E. Rose and J. L. Perkins *Amer. Ind. Hyg. Ass. J.* 43, 605- 621 (1982).

10. Pro-Tek Systems, Inc., 3M and Dupont all manufacture these devices which are described in reference 9.

11. R. Ellersick, *Research on Personnel Dosimeters to Measure Hydrazine Fuels in Air*, Air Force Report SAM-TR-79-22 (1979).

12. P. A. Taffe, S. L. Rose-Pehrsson, and J. R. Wyatt, *Material Compatibility with Threshold Limit Values of Monomethyl Hydrazine*, NRL Memorandum Report 6291 (1988).

13. S. Dushman and J. M. Lafferty, Ed., *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, New York, 1962), p 82-86.

14. G. Lewin, *Fundamentals of Vacuum Science and Technology* (McGraw-Hill, Inc., New York, 1965), p 16-18.

15. C. O. Bennett and J. E. Myers, *Momentum, Heat, and Mass Transfer,* 3rd Ed, (McGraw-Hill, Inc., New York, 1982), Chap. 32.

16. A. P. Altshuller and I. R. Cohen, *Anal. Chem.* 32, 802-810 (1960).

17. S. L. Rose and J.R. Holtzclaw, *A Critical comparison of Commercially Available Hydrazine Detectors*, NRL Report 8848, Naval Research Laboratory, Washington, DC, March 19, 1985.

18. E. C. Olson, *Anal. Chem.* 32, 1545-1547 (1960), this procedure has been miniaturized by both NASA, WSTF and NRL personnel and will be the subject of a future report.

19. Reference 15, p121.

20. The badges were made by drilling holes in the top of Fluoroware (Fluoroware, Inc., Chaska, Minn.) cassettes designed for holding silicon wafers. These cassettes were molded from Kel-F (3-M trademark for chlorotrifluoroethylene polymer).

21. C. M. Hawkins, S.L. Rose, and J.R. Wyatt, "A Passive Dosimetry Method for Determining Hydrazine in Air," CP1A 436, *Proceedings of the 1985 JANNAF Safety and Environmental Protection Subcommittee Meeting*, (Monterey, CA, 4-8 November 1985) Naval Postgraduate School, November 1985.

22. Maryland Blue Print Company of Columbia, Maryland (stock # D-F3).

23. This material is available from a variety of scientific supply companies.

24. J. R. Holtzclaw, S. L. Rose, J. R. Wyatt, D. P. Rounbehler, and D. H. Fine, *Anal. Chem.* 56, 2952-2956 (1984).

25. P. A. Taffe, S. W. Brown, A. R. Thurow, J. C. Travis, S. L. Rose-Pehrsson, and J. R. Wyatt, *Field Evaluation of a Passive Sampling Device for Hydrazines in Ambient Air*, NRL Memorandum Report 6613 (1990).

26. Reference 15, p564.

27. D. F. Eggers, N. W. Gregory, G. D. Halsey, and B. S. Rabinovitch, *Physical Chemistry*, (John Wiley and Sons, Inc., New York, 1964), Chap. 18.

28. B. E. Shaefer, "The Astrophysics of Suntanning", *Sky and Telescope*, 75, 595-596 (1988).